DEPARTMENT OF ENVIRONMENTAL AFFAIRS AND TOURISM

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INTRODUCTION TO TYPES AND SOURCES OF AIR POLLUTANTS

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ACRONYMS

BTX	Benzene, Toluene and Xylene
CO	Carbon Monoxide
CO_2	Carbon Dioxide
GHG	Greenhouse Gas
NMHC	Non-Methane Hydrocarbon
NO	Nitric Oxide
NO_2	Nitrogen Dioxide
NOx	Oxides of Nitrogen
O_3	Ozone
PAN	Peroxyacetylnitrate
Pb	Lead
PM	Particulate Matter
$PM_{2.5}$	Particulate Matter smaller than or equal to 2.5μm in diameter
PM_{10}	Particulate Matter smaller than or equal to 10μm in diameter
TSP	Total Suspended Particulates
SO_2	Sulphur Dioxide
VOC	Volatile Organic Compound

GLOSSARY OF TERMS

Ambient air
Considered to be the air in the environment excluding indoor air.

Anaerobic
Refers to processes occurring without the presence of oxygen.

Anthropogenic sources
Pollution sources that are related to human activities.

Biogenic sources
Emission of a range of pollutants from soils and vegetation.

Combustion
Burning, or rapid oxidation, accompanied by release of energy in the form of heat, light and waste products.

Dimethylsulphide
An organic compound containing sulphur that is produced in the ocean by certain phytoplankton species.

Emission
Pollution discharged into the atmosphere from a range of stationary and mobile sources. These include smokestacks, vents and surface areas of commercial or industrial facilities; residential sources; motor vehicles and other transport related sources.

Environment
The surroundings within which humans exist and that are made up of (i) the land, water and atmosphere of the earth; (ii) micro-organisms, plant and animal life; (iii) any part or combination of (i) and (ii) and the interrelationships among and between them; and (iv) the physical, chemical, aesthetic and cultural properties and conditions of the foregoing that influence human health and well-being (definition from the National Environmental Management Act - NEMA)

Greenhouse Gas
Any gas that absorbs infra-red radiation in the atmosphere. Greenhouse gases include water vapor, carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), halogenated fluorocarbons (HCFCs) ozone (O_3), perfluorinated carbons (PFCs), and hydrofluorocarbons (HFCs).

Line source
An array of pollutant sources along a defined path that can be treated in dispersion models as an aggregate uniform release of pollutants along a line.

Natural sources
Pollution sources that are related to natural processes as opposed to those which are due to human activities.

Nucleation
Nucleated particles are those that form from the gaseous phase.

pH
pH is a measure of the activity of hydrogen ions (H^+) in a solution and, therefore, its acidity or alkalinity. The pH value is a number without units, usually between 0 and 14, where 7 is neutral and greater than 7 is more basic and less than 7 is more acidic.

Point source
A pollutant source that can be treated in a dispersion model as though pollutants were emitted from a single point that is fixed in space.

Priority pollutant
A pollutant that has been identified in the AQMP as requiring intervention to reduce ambient air quality levels. Factors that may influence whether a pollutant is identified as such include: its toxicity; the volume of emissions; or the proximity of the emission relative to sensitive receptors.

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1. INTRODUCTION

The atmosphere is composed of a number of gases and particulate matter that exist in different concentrations. The natural atmosphere comprises nitrogen (78.1%), oxygen (20.9%), argon (0.9%), carbon dioxide (0.03%) and a number of gases that naturally exist in trace amounts including neon, helium, methane, hydrogen, ozone, carbon monoxide, sulphur dioxide and water vapour (Singh H.B, 1995).

Human activities as well as natural processes are capable of emitting gases and particulates into the atmosphere that will result in deviations from the natural atmospheric composition. The type of air pollutant that is emitted and the extent and nature of its impact depends largely on the characteristics of the source, the physical and chemical nature of the pollutant and the capability of the atmosphere to disperse and dilute the pollutant.

The objective of this book is to provide a broad understanding of air pollution source types and to provide an introductory understanding of different air pollutants. Air pollution sources are discussed in broad categories of anthropogenic and natural with the focus falls on the criteria pollutants.

2. SOURCES OF AIR POLLUTION

Air pollution sources may be divided into the two broad categories of anthropogenic and natural sources.

Anthropogenic sources arise as a result of human activity. Perhaps the most common and recognisable activity is that of industry, which encompasses manufacturing (e.g. oil refineries, steel mills, cement factories etc.), power generation as well as service related activities (e.g. dry cleaners or fast food outlets). Others include transportation (motor vehicles, aircraft, etc) relying on combustion engines, agriculture (e.g. crop burning, ploughing), mining, fossil fuel burning for cooking and heating and refuse burning. Emissions of air pollutants from the most common anthropogenic sources, especially industrial sources, have been fairly well quantified in the form of emission factors which are often used for planning and air quality management purposes, see the following two web sites:

- US EPA Clearinghouse for Inventories and Emission Factors at http://www.epa.gov/ttn/chief/ap42/index.html,
- European Integrated Pollution Prevention and Control Bureau at http://eippcb.jrc.es/pages/FActivities.htm

Natural sources are associated with the earth's natural processes. They can often release large amounts of pollutants into the atmosphere, in a relatively short period of time, e.g. volcanoes or dust storms. Other, more continual sources include grazing animals (especially if they occur in large numbers), vegetation, lightning and microbial activity in soils. Biogenic sources are a

subset of natural sources and include only those sources that result from some sort of biological activity. Examples of biogenic sources include vegetation and microbial activity in soils.

Anthropogenic and natural sources may be categorised further according to the physical nature of the source. The common classification is discussed here:

2.1 Stationary Sources

Stationary sources are those that remain at one locality while emitting pollutants. They are usually associated with fixed structures such as buildings, and often emit pollutants in qualities and quantities that remain fairly steady over time. An example is a smoke stack or an extractor outlet.

Stationary sources may be divided into the following classes:

> ***Point sources*** have fixed geographical coordinates; they are generally elevated above ground level and have a small exit diameter relative to the height of the source. The term point source is commonly used to refer to industrial smoke stacks and flare stacks (at oil refineries). Typically, point sources are seen as large emitters.
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> ***An area source is*** a term used to describe sources that have relatively large horizontal dimensions (unlike a point source). Many smaller stationary sources located together whose individual emissions may be low but whose collective emissions can be significant are often grouped together as an area source. Geographically they are considered as an area, and emissions are represented as a collective value. In such a case, an example is the boundary of a residential area where a number of braziers (mbaulas) are individually emitting pollutants. Mines and quarries are regarded as area sources.
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> ***Fugitive sources*** are elusive sources that are difficult to identify. Examples would include leaking valves, pipes and pumps and storage piles that release pollutants into the atmosphere. Such fugitive emissions can often only be quantified using special measuring or estimation techniques.
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> ***Volume sources*** are sources that have relatively large horizontal and vertical dimensions. Examples include material stock piles or mine dumps where wind may liberate particulate matter or dust.

2.2 Mobile Sources

Mobiles sources are mostly associated with transportation and internal combustion engines with pollutants being emitted along the path taken. These sources include motor vehicles (cars, trucks, buses etc.) as well as off-road

vehicles (aeroplanes, boats, farm machinery). It is also possible for an unpaved road to be termed a mobile source since the distribution of emissions (primarily dust) is similar to that of a motor vehicle, i.e. the pollutants are emitted along a path.

3 TYPES OF AIR POLLUTANTS

Types of air pollutants can vary vastly according to attributes such as their physical and chemical composition, their toxicity and reactivity. Classification of pollutant types can therefore be made. Typical classifications are:

Primary Pollutant: These are air pollutants that are emitted directly into the atmosphere from its respective source. An example is carbon monoxide (CO) emitted from a motor vehicle exhaust or sulphur dioxide (SO_2) emitted from an industrial stack.

Secondary Pollutant: These are pollutants that are formed within the atmosphere as a result of various reactions between different primary pollutants or with natural constituents in the atmosphere. An example is ozone (O_3) which forms through the reaction within the atmosphere between oxides of nitrogen (NO_x) and hydrocarbons in the presence of sunlight.

3.1 Criteria Pollutant

Criteria pollutants are regarded as the common air pollutants for which national ambient air quality standards or guidelines have been set. The six criteria pollutants in the United States, the European Union and South Africa are: carbon monoxide (CO), nitrogen oxides (NO_x), sulphur dioxide (SO_2), ozone (O_3), particulate matter and lead (Pb). The key characteristics of these pollutants and the common sources are discussed here:

Carbon Monoxide (CO)

CO is a colourless, odourless and tasteless gas. It is slightly denser than air and slightly soluble in water. It is often found as a primary pollutant, and can be oxidised (via the hydroxyl radical) to form Carbon Dioxide (CO_2). This occurs rapidly in the atmosphere, giving CO a relatively short residence time, though if emissions are intense over shorter periods of time, build-up is possible (e.g. within the urban or industrial context). CO is poisonous in high concentrations and in confined spaces it can result in asphyxiation and death.

CO is a product of incomplete combustion of fossil fuels. Though predominantly formed in internal combustion engines of motor vehicles, any combustion of carbon based material has the potential to release CO (e.g. domestic use of biofuels, biomass burning and incineration of

solid wastes). Industrial processes may also lead to the production of CO. CO generated by the use of biofuels has become significant in South Africa as this is the only source of energy available for people living in rural areas.

CO can arise from incomplete combustion of carbon based materials in the natural environment, such as veld and forest fires. Volcanoes can be a significant source of CO. Besides combustion, natural reactions within the atmosphere may also lead to the formation of CO by the oxidation of other carbon based gases, e.g. methane. Decomposition of organic material within soils and forest floors can result in the release of CO as well.

Oxides of Nitrogen (NO_x)

NO_x is a term commonly used to refer to the combination of nitric oxide (NO) and nitrogen dioxide (NO_2). NO is a colourless and odourless gas. It is insoluble in aqueous solutions. It may rapidly be transformed into nitrogen dioxide (NO_2); NO_2 has a distinctly acidic odour, and at ambient temperatures is in equilibrium with its dimer (N_2O_4), which is reddish brown in colour (associated with brown haze). NO_2 is a strong oxidising agent in the atmosphere and may form nitric acids. NO_x can react with the moisture in the respiratory system to form nitric and nitrous acids. The effects include impaired cell function and respiratory illness. NO_x also reacts with water in the atmosphere and can contribute to the formation of acid rain. NO_x is an important pre-cursor gas in the formation of ozone.

NO_2 and NO are formed simultaneously in combustion processes and other high temperature operations such as metallurgical furnaces, blast furnaces, plasma furnaces, and kilns. The ratio between the gases depends on the temperature of the process, with higher temperatures leading to more NO_2. NO_x can also be released from nitric acid plants and other types of industrial processes involving the generation and/or use of nitric acid. NO_x may be formed naturally by the process of denitrification by anaerobic bacteria in soils and plants. Lightning is a rich source of NO_x in the atmosphere. NO_x forms during the discharge and the rapid cooling of air after the electric discharge.

Sulphur Dioxide (SO_2)

SO_2 is a colourless gas that is moderately soluble in water. It has a pungent odour, similar to that of a burning match. Dominant sources of SO_2 include fossil fuel combustion from industry and power plants. SO_2 is emitted when coal (especially lower grade) is burnt for energy. Domestic coal burning can thus also result in the release of SO_2. The combustion of liquid fuels may also results in SO_2 emissions, depending on the source of the fuels. Diesel engines tend to emit more SO_2 than petrol engines, as petrol usually has lower sulphur content than diesel fuel. Mining processes that require smelting of mineral ores

can also result in the production of SO_2 as the desired metals are often found as sulphides within the ore.

Natural heating of minerals that are rich in sulphur will also lead to the release of SO_2. Such is the case with any volcanic activity. If the surrounding rock contains sulphides, high temperatures will aid in the production and release of SO_2. Volcanic eruptions often result in massive release of SO_2 over a very short period of time. This can even affect global SO_2 concentrations within a few weeks. The oxidation of biologically produced dimethylsulphide in oceans and soils and hydrogen sulphide (H_2S) may also lead to emissions of SO_2.

Like NO_x, SO_2 reacts with cell moisture in the respiratory system to form sulphuric acid. This can lead to impaired cell function and effects such as coughing, broncho-constriction, exacerbation of asthma and reduced lung function. SO_2 has the potential to form sulphurous acid or sulphuric acid (although formation of the latter is slower) in the atmosphere via oxidation by the hydroxyl radical. The sulphuric acid may then dissolve in water droplets and fall as precipitation. This may decrease the pH of rain water, altering any balance within ecosystems and can be damaging to man-made structures (the so-called “acid rain”).

Ozone (O_3)

Ozone is a colourless gas, but appears slightly purple at higher mixing ratios, and carries a harsh odour. Ozone occurs naturally in the lower stratosphere as the ozone layer, which protects the earth from shortwave ultraviolet radiation. Near the earth’s surface ozone is a secondary pollutant and is a major constituent of photochemical smog.

The formation of ozone relies greatly (if not exclusively) on the availability of NO_x, hydrocarbons and sunlight. Thus ozone may not be related directly to any source, but rather it may be associated with the sources of its precursor gases (NO_x and hydrocarbons). Ozone may also reach the lower troposphere from the stratosphere, mostly associated with deep frontal systems or with deep convective storms.

Ozone is a very reactive gas and is a strong oxidant and is associated with a number of health effects. These include respiratory system effects such as coughing, aggravation of asthma and reduced lung function.

Lead (Pb)

Lead is a metal that occurs naturally in the environment. It was used as an anti-knock agent in gasoline before the advent of unleaded fuel, in the manufacture of some types of paints, solders, piping and in the manufacture of batteries. Lead has a low boiling point and as such is vaporised easily during combustion processes. It can then condense

on to the surface of fine particles. Lead compounds can be present in the atmosphere in a solid form (lead phosphate, lead chloride, and lead bromide) or in a gaseous form as alkyl lead that has evaporated from petrol. The lifetime of a lead particle in the atmosphere is ~7-30 days.

Lead emissions are predominantly anthropogenic and the sources include the combustion of leaded fuels, mining and smelting of lead, and solid waste disposal. Lead exposure may also occur by use of lead based paints and solders and lead piping. Natural sources include wind blown dust and volcanoes.

Lead accumulates in the human body and is associated with neurological effects, blood disorders, immunological effects, gastrointestinal effects and effects of the reproductive system. Children are particularly at risk. Lead has systematically been phased out of South African gasoline which is not manufactured or sold in the country from January 2006.

Particulate Matter (PM)

Particulate matter is a broad term used to describe the fine particles found in the atmosphere, including soil dust, dirt, soot, smoke, pollen, ash, aerosols and liquid droplets. The most distinguishing characteristics of PM are the particle size and the chemical composition. Particle size has the greatest influence on the behaviour of PM in the atmosphere with smaller particles tending to have longer residence times than larger ones. PM is categorised, according to particle size, into TSP, PM_{10} and $PM_{2.5}$.

Total suspended particulates (TSP) consist of all sizes of particles suspended within the air. High TSP concentrations will lead to nuisance effects such as settling on houses, deposition on and discolouration of buildings, and reduction in visibility.

PM_{10} describes all particulate matter in the atmosphere with a diameter equal to or less than 10 micrometers. Sometimes also referred to as inhalable particles, they are generally emitted from motor vehicles (primarily those using diesel engines), factory and utility smokestacks, construction and mining sites, tilled fields, unpaved roads, stone crushing, and burning of wood. Natural sources include sea spray, windblown dust and volcanoes. These particles tend to have relatively short residence times as they settle out rapidly. Unless there are strong winds, PM_{10} is generally found relatively close to the source. PM_{10} are sufficiently small to enter the lung.

$PM_{2.5}$ describes all particulate matter in the atmosphere with a diameter equal or less than 2.5 micrometers. They are often called fine particles, and are more related to combustion (motor vehicles, smelting, incinerators), than mechanical processes, as is the case with PM_{10}. It is

also possible for fine particles to be formed within the atmosphere in three ways:

- Heterogeneous nucleation of vapour phase material, i.e. particles that form from the gas phase.
- Homogeneous nucleation of vapour phase material, i.e. gaseous molecules aggregate or cluster together without the aid of an existing surface, forming a new particle.
- Atmospheric reactions of gases to form vapours that homogeneously and heterogeneously nucleate to form particles.

$PM_{2.5}$ is sufficiently small to enter the alveoli in the lungs. $PM_{2.5}$ tends to stay suspended in the atmosphere for long periods of time (in the order of months), and thus have the ability to be transported over large distances.

3.2 Other air pollutants

Carbon Dioxide (CO_2)

CO_2 is a colourless gas that is denser than air. When inhaled at high concentrations it produces a sour taste and a stinging sensation in the nose and throat. CO_2 exists naturally in the atmosphere, but its concentration has increased significantly since the onset of the industrial revolution and it is now considered to be the most important Green House Gas (GHG). It is fully oxidised, and therefore not very reactive. CO_2 is slightly soluble in water, and it forms a weak acid (carbonic acid).

CO_2 sources are generally related to the combustion of fossil fuels. It is often the case that fuels contain impurities, and these are released along with CO_2. Industrial sources include hydrogen and ammonia production, and any acid neutralisation process that utilises calcium carbonate (limestone). Other sources may include carbonated drinks, fire extinguishers and numerous areas of the food industry.

Natural sources make up a large portion of CO_2 contribution in the atmosphere. These sources are widespread and can release large amounts of CO_2 in a short period of time. An example of such a source is a volcano (outgassing events). Various rock types contain carbonated minerals, which when in contact with acidic water, may release CO_2 into the atmosphere. CO_2 is also released by vegetation during the night, though it takes in CO_2 during the day. The destruction of rain forests releases the carbon content of the vegetation in the form of CO_2.

Volatile Organic Compounds (VOCs)

The term VOCs is used to include many of the organic compounds emitted into the atmosphere, and has hydrocarbons (compounds

composed of only Carbon and Hydrogen) as a subcategory. The key characteristic of VOCs is that they have high vapour pressures (tend to evaporate easily). They are therefore volatile and some of them react readily. VOCs, together with NO_x and sunlight, are key to ozone formation and other compounds of photochemical smog, such as peroxyacetylnitrate (PAN). Due to their chemical composition and structure, VOCs can be classified into numerous groups, of which the following are considered to be the most important:

Alkanes – These consist of single bonds between carbons and follow the general formula C_nH_{2n+2}. Examples are methane propane and butane. Methane is the second most important Greenhouse Gas (next to CO_2) on a global basis. It has a low photochemical activity and is thus separated from other hydrocarbons which are then given the term non-methane hydrocarbons (NMHC). Primary sources of alkanes are natural gas and oil. Natural gas is mostly made up of methane and ethane, with a bit of propane and butane. Alkanes also evaporate from oil. Combustion of higher order hydrocarbons may result in the emission of alkanes.

Alkenes – These contain double bonds between carbons and follow the general formula C_nH_{2n}. Examples are ethane, propene and butene. Alkenes react rapidly with the hydroxyl radical and are important in ozone formation.

Aromatics – These consist of a benzene ring with additions. Benzene is thus the simplest aromatic hydrocarbon. Other aromatics include Toluene and Xylene. Benzene, Toluene and Xylene are often collectively called BTX. Aromatic hydrocarbons probably make the most significant contribution to the creation of ozone and other photo-oxidants in the atmosphere. Sources of aromatics are almost entirely anthropogenic, and include petrol combustion and refining, detergent production, biomass burning and lacquers and glues.

Oxygenated hydrocarbons – These consist of alcohols, aldehydes, ketones and acids. They are commonly found as secondary pollutants, though primary sources could include motor vehicles and solvent vapours. Formaldehyde is the most abundant aldehyde and can produce ozone precursors through various reactions. Methanol and ethanol (both alcohols) also contribute to ozone production. Methanol can produce formaldehyde, and ethanol produces acetaldehyde (a precursor to PAN).

Terpenes – These consist of naturally occurring hydrocarbons such as isoprene. Sources include forests, biomass burning, the use of scented deodorants and fabrics. They are very reactive and are thus readily removed from the atmosphere, and can contribute to ozone formation.

Methane (CH_4)

Methane is the simplest hydrocarbon. It is colourless, flammable, and in its pure form, odourless. Often called natural or marsh gas, it is naturally found mixed with other hydrocarbons (ethane, butane, propane, etc.) and various organic sulphur compounds, which give it an unpleasant odour. Methane may also be synthetically produced by the distillation of bituminous coal and by heating a mixture of carbon and hydrogen and is used to manufacture methanol, formaldehyde and carbon tetrachloride. Methane is primarily used as a fuel and produces less carbon dioxide per unit of energy than other fossil fuels. It is also a GHG and can absorb infra-red radiation ~23 times more efficiently than CO_2 (CH_4 is the second most important GHG, next to CO_2 on a global basis).

Sources of methane include combustion of fossil fuels, biomass burning, domestic sewage, digestive tracts of ruminant animals and decomposition of organic matter by bacteria under anaerobic conditions.

Methane is an asphyxiant and flammable and therefore could prove hazardous in confined spaces.

Hydrogen Sulphide (H_2S)

Hydrogen Sulphide is a flammable gas that is slightly heavier than air; it is colourless and is toxic. It carries an offensive odour, similar to that of a rotten egg. It can at times be corrosive to metals, tarnishing silver and making steel brittle while forming metal sulphides. It is also oxidised within the atmosphere to form SO_2, thereby increasing SO_2 levels.

Natural sources include volcanoes and other geothermal processes, decomposition of organic matter and bacterial reduction of sulphates in anaerobic conditions. Anthropogenic sources include pulp and paper industry, coke ovens, sewage plants and oil refineries.

H_2S is highly toxic. It is considered a broad-spectrum poison, meaning that it can poison several different systems in the body, although the nervous system is most affected. Breathing hydrogen sulfide may paralyze the olfactory nerve making it impossible to smell the gas after an initial strong exposure.

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